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# **Final Report**

**Air Force Grant # F49620-01-1-0424**

**Miniaturization Science for Space: Lubrication of  
Micro-Electro-Mechanical Systems (MEMS) for Space Environments**

For the period: 06/01/01-11/31/2005

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## **2. Objectives**

The objective of this research program is to develop a fundamental understanding of the merits and detriments of a number of specific approaches to lubricating MEMS devices, allowing for their successful operation in space environments. The program seeks to determine the effects of environmental parameters experienced by satellite mechanisms in order to further screen candidate systems for specific aerospace missions. The approach entails measurements of surface composition and structure by a number of molecularly specific surface analytical techniques and the subsequent correlation with tribological measurements. As lubrication schemes for MEMS devices represent an active area of development, this program is investigating a range of materials and interfaces with respect to operation in a space environment. The program seeks to understand the impact of environmental variables such as pressure, temperature, and the presence of atomic oxygen and hard radiation on the range of candidate materials and interfaces. Together, these data aim to provide a complete picture of the molecular issues associated with the success and failure of interfacial motion of MEMS devices under a wide range of conditions.

## **3. Status of Effort:**

This program has focused on the influence of temperature and vacuum pressures on a number of tribological materials considered as candidates for incorporation into MEMS fabrication. These materials have included silane-based alkyl self-assembled monolayers (SAMs), diamond like carbon (DLC) films and SiC. Fundamental measurements performed on the operational length scale of MEMS devices (nanometer to micron) demonstrate a significant influence of these environmental parameters.

In addition, UHV friction measurements on model surfaces have sought to establish a systematic understanding of the temperature dependence of the forces acting at sliding interfaces. This work has considered the frictional properties of a series of single crystal surfaces in the absence of wear or interfacial chemistry. The results of these measurements have allowed the consideration of a number of fundamental contributing effects to the temperature dependence of sliding friction.

## **4. Accomplishments/New Findings**

- **Fundamental Studies of Temperature-Dependent Friction**

The influence of temperature on the frictional properties and molecular structure of hexadecanethiol self-assembled monolayers (SAMs) adsorbed on gold has been measured by atomic force microscopy (AFM) in a vacuum environment. The frictional response of hexadecane thiol films decreases significantly when heating the as-deposited SAM film from room temperature to 330K, with a corresponding increase in surface order. The changes observed during the first heat treatment are irreversible, with the room temperature frictional response lowered by approximately a factor of four. However subsequent heating cycles produce a reversible change in interfacial friction for temperatures up to 350K, with interfacial friction increasing

with increasing temperature. Further heating the SAM film above 370 K produces a significant and irreversible increase in friction. At 400 K, the lattice-resolved structure of the Au(111) surface is observed, indicating the instability and initial stages of desorption of the alkanethiol film at this temperature. Following surface anneals to 500 K, only small three-dimensional islands of residual thiol are observed in large-scale topographic images and the frictional properties largely reflect those of bare gold. The reversible increase in the frictional properties of the hexadecanethiol film with increasing temperature is ascribed to a decrease in the molecular order and the effective density of the film. Above the temperature threshold for film damage, the irreversible increase in frictional response is ascribed to energy being dissipated through plowing and displacement of the film. The range of influences of temperature on the frictional properties of these alkanethiol films illustrates the complex relationship between friction and film structure on the molecular level. While alkanethiol films are not compatible with current MEMs packaging procedures due to the high temperatures, these studies do reflect the potential for significant variations in interfacial friction when using monolayer based lubricants.

- **Temperature Dependent Friction of Titanium Nitride Coatings**

Titanium nitride TiN is currently used within the microelectronics industry (VLSI technology) as a diffusion barrier. Titanium nitride also represents a widely used hard coating. There exists the potential for generating within the framework of existing technologies protective TiN coatings on MEMs surfaces in order to prolong device lifetime. To this end, the frictional properties of TiN(100) films have been measured by variable temperature atomic force microscopy in vacuum. The room temperature friction decreases significantly, relative to that of the native oxide of TiN, after sputtering and annealing. It further decreases after exposing the sputtered and annealed film to oxygen. In addition to these differences, the three surface modifications (sputter cleaned, annealed, and oxidized) show distinct temperature dependences. The friction of all samples increases with temperature over the temperature range 300-800 K, however the sputter cleaned surface exhibits the greatest rate of increase over this range. The results show the modification of sputtering and annealing, as well as oxygen exposure can lower the surface friction of TiN films at elevated temperatures: the sputtered and annealed film exhibited low friction up to 500K, while the oxygen exposed film exhibited low friction up to 600K.

- **Temperature Dependent Friction of Model Interfaces**

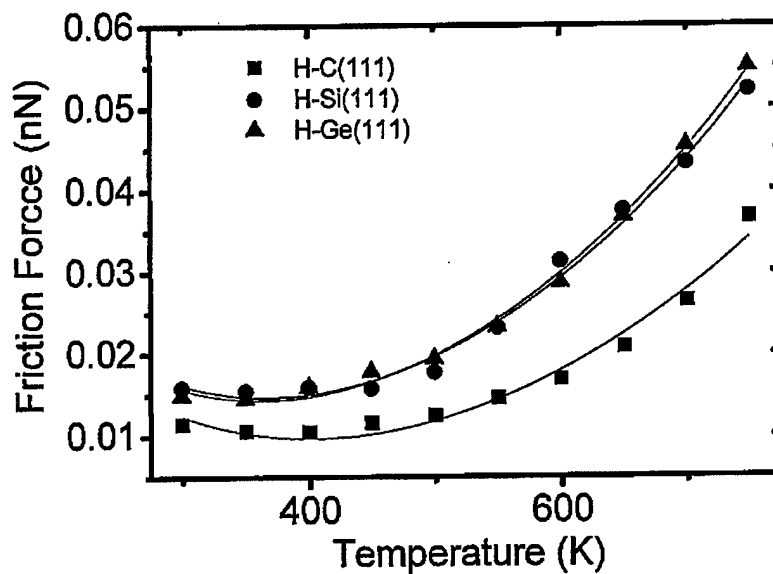
The temperature dependencies of friction have measured as a function of temperature (300K-750K) by variable temperature atomic force microscopy on hydrogen terminated diamond(111), silicon(111) and germanium(111) held in an ultrahigh vacuum environment. These samples present the exact same surface structure and very similar surface chemistries and have allowed investigations of the fundamental origins of temperature dependent friction in the absence of wear. The friction of the three samples increase with temperature, and the temperature dependencies can be explained by the theory of phonon energy dissipation.

The experiments were performed in a UHV chamber at a pressure of  $10^{-10}$  Torr. Low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) (Omicron Instruments) were used to evaluate surface structure and composition. In this study, the interfacial friction was measured using a beam deflection AFM, and a same  $\text{Si}_3\text{N}_4$  tip was used for all AFM measurements. Lateral and normal forces,  $F_L$  and  $F_N$ , were detected in a number of areas across the surface to get the average friction properties, at a constant scanning velocity of 400nm/s.

The temperature dependence of friction forces on H-C (111), H-Si (111) and H-Ge (111) obtained under normal load of 10nN are shown in Fig.1. It can be seen the friction force increases with temperature for all three samples. These results were obtained in the absence of significant contributions from changes in interfacial adhesion or in the force constants of the cantilever with changing temperatures. We propose that the temperature dependence of the interfacial friction at these largely unreactive interfaces can be described in terms of the following equation, derived from the velocity dependent model of friction developed by Yi Sang et. al.

$$F = F_c - F_1 T^{2/3} |\ln(F_2 / T)|^{2/3}$$

Additional work is currently underway to further verify this model. These experiments entail the use of additional samples as well as investigations at cryogenic temperatures. The aim of these studies is to be able to describe the temperature dependence of interfacial friction in terms of specific elemental properties.



**Figure 1.** The interfacial friction measured between a silicon nitride probe tip and the three similar surfaces reveal a systematic increase in interfacial friction with increasing temperature.

- **Frictional Performance of Self-Assembled Monolayers on Silicon Surfaces**

The temperature dependence of the various SAM film systems deposited on Si has been investigated on the molecular scale with atomic force microscopy. Films synthesized through a number of different procedures were first investigated at room temperature under ambient conditions. Deposition procedures involved the vapor deposition of a C<sub>18</sub> alkylsilane, solution deposition of a C<sub>18</sub> alkylsilane, catalyzed reaction of an n-alcohol with silicon and silicon oxide surface from isooctane solution, and direct attachment of alkyl chains to hydrogen terminated silicon surfaces through the addition reaction of the corresponding alkene. The frictional properties of the resulting chemically equivalent films demonstrated a clear dependence on the local order of the organic monolayer, with higher friction being correlated with lower order within the film. The predominant difference in the film structure involves the size of that anchoring head group.

In addition to the revealing measurements at room temperature, the frictional properties were investigated in a vacuum environment as a function of temperature over the range 300-800 K. Over this range, all films exhibited significantly superior tribological properties (mostly related to wear) in comparison to the alkanthiol films on gold described above. Again a correlation between lower friction and higher film order and density was observed at all temperature. A 2-3 fold increase in interfacial friction was observed for the highest quality films over the 300 to 600 degree window. A threshold to film decomposition was observed near 750 K, consistent with previous surface analytical measurements. Decomposition was correlated with a significant increase in interfacial friction. Films deposited from alkyltrialkoxysilane solutions exhibited a greater relative rise in friction with increasing temperature relative to those films deposited from alcohols and alkenes.

Among these films, several general observations were made: films deposited from alkyltrialkoxysilane solutions exhibited a greater relative rise in friction with increasing temperature relative to those films deposited from alcohols and alkenes. Work in the most recent funding year has sought to establish the origin of these differences. Initially, contact angle measurements with a range of contacting liquids were evaluated as a testing protocol. Unfortunately, this approach did not prove reliable in distinguishing differences between the films synthesized by different procedures. Instead, surface vibrational spectroscopy has been explored as a means for characterizing the character of the films. In the past, PM-IRRAS has been used by our group to establish a correlation between the local disorder (with respect to trans-gauche defects) of a film and its frictional properties. While initial results have been obtained on a few samples, silicon has proved to be challenging as a substrate in experiments involving infrared radiation.

- **Pressure Dependent Measurements of Interfacial Friction**

Again using the ultrahigh vacuum AFM, we have explored the frictional properties of two hard materials that represent potential coatings in MEMs applications- diamond like carbon (DLC) and silicon carbide (SiC). The objective of this series of measurements was to demonstrate the range of frictional forces that could be expected with variations in

ambient pressure. Using a standard silicon nitride probe tip, the friction of these two surfaces was measured at  $1 \times 10^{-10}$  torr, 1 atm  $N_2$ , 1 atm dry air, and 1 atm air (50% relative humidity (RH)). As seen in figure 2, a systematic increase in friction was observed with increasing pressure. A survey of the literature indicates that such a dependence has been observed before for certain materials and is thought to relate to the role of water condensation at the tip-surface contact; however little direct evidence exists to support this claim. Additional studies are now being carried out in our laboratory on a broader range of samples (hydrophobic to hydrophilic) to more fully explore the role of water in the pressure-dependent results recorded for these samples. Nonetheless, these results clearly demonstrate the range of variations that can be expected in taking MEMs devices into a space environment.

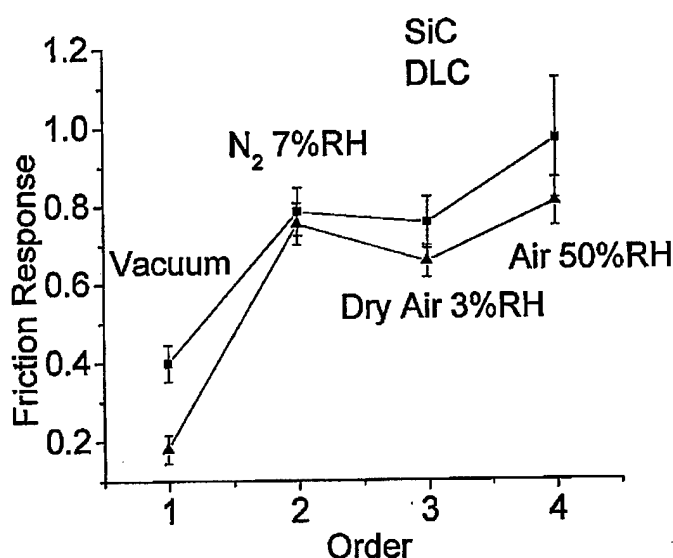


Figure 2. Pressure dependent friction measurements reveal a significant increase in friction with increasing ambient pressure and atmospheric water.

#### • Time of Flight Mass Spectrometric Studies of Gas-Surface Interactions

In the past year significant effort has been applied to the development of time of flight capabilities for mass spectrometric studies of gas-surface reactions. Funding for the purchase of a portion of the instrumentation has been supplied as a supplement to the current program. The use of TOF-MS techniques will provide unique opportunities for the study of surface degradation of lubricants at elevated temperatures and the mechanistic pathways of vapor phase lubrication.

The TOFMS constructed at UH consists of an ionization source, flight tube, a microchannel plate detector (MCP), and a corresponding set of power supplies: one for the pulsed electron gun; a second one for the pulsed repeller; and a third for high voltage. A signal triggers a pulsed electron beam (70 eV) that lasts 8  $\mu s$  and ionizes the gas phase molecules inside the ionization source. A 3  $\mu s$  delay is followed by a repeller pulse (128

V, 8  $\mu$ s) that pushes the ions into the flight tube, which is held at 1850 V. The TOF of an ion is determined by the following equation:

$$t = L * [m / (2 * z * V)]^{1/2}$$

where L is the flight tube length, m is the ion mass, z is the ion charge, and V is the flight tube voltage. The MCP detector converts an ion to an electron pulse and this pulse is then amplified 10 times through a preamplifier. After the amplification, a DSA digitizes and accumulates the signals as waveform. The DSA digitizes signals every 2 ns and it has a very short dead time between scans (< 1  $\mu$ s). Compared to the typical 1 to 10 ms of dead time for a digital oscilloscope, this short dead time of the DSA dramatically reduces the data acquisition time. This configuration allows for a TOFMS scan to take place in 52  $\mu$ s: 8  $\mu$ s for an ionization pulse, a 3  $\mu$ s delay, 40  $\mu$ s of data acquisition that start with a repeller pulse, and 1  $\mu$ s dead time. Accumulation of 10,000 scans of the full mass range (0 to 5,000 amu), to obtain good signal-to-noise ratio, takes 0.6 s.

To date, the system has been designed and installed and time dependent measurements of background gases have been performed (Fig. 3). Unfortunately, the latest investigations have revealed that the used condition of the TOF-MS will require additional funds to bring the instrument up to full operation conditions. Funds are currently being sought for this purpose.

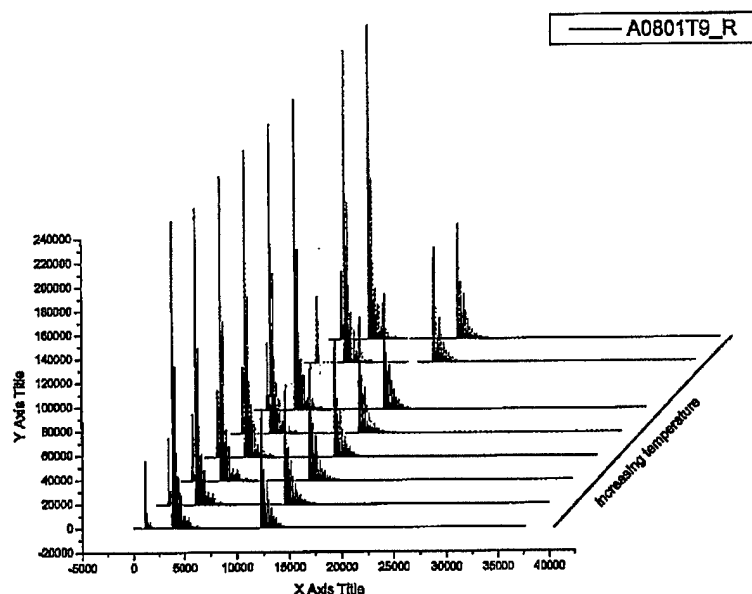


Figure 3. Time resolved TOF-MS spectra collected with the newly constructed instrumentation.

## 5. Personnel Supported

University of Houston

Karen Fortune, Graduate student

Mr. Gang Liang, Graduate student  
Dr. Zhongqing Wei, Postdoctoral Fellow  
Dr. Xueying Zhao, Postdoctoral Fellow  
Dr. Scott S. Perry, Professor

## 6. Publications and Presentations

### *Publications*

Yang, Xinju; Perry, Scott S.. **Friction and Molecular Order of Alkanethiol Self-Assembled Monolayers on Au(111) at Elevated Temperatures Measured by Atomic Force Microscopy.** *Langmuir* (2003), 19(15), 6135-6139.

### *Presentations (invited)*

Scott S. Perry "The Influence of Molecular Structure and Composition on the Frictional Properties of Organic Thin Films", CSEM, Neufchatel, Switzerland, October 2001

Scott S. Perry "Uncovering the Molecular Details of Buried Interfaces: Apply Surface Science Tools to Tribological Problems", ETH-Zurich, June 2003

Scott S. Perry, "The influence of temperature on the frictional properties of model interfaces" University of Basel, Basel Switzerland, July 2003

## 7. Interactions/Transitions

Attended the kick-off meeting for the MURI - 2001 MATERIALS  
DEGRADATION/PASSIVATION IN THE SPACE ENVIRONMENT

June 18-19, 2001

Ohio Aerospace Institute

Discussion of mechanisms of materials oxidative degradation.

Efforts have been made to establish a closer tie to the MEMs program at AFRL/MLBT. Initial efforts will focus on the common use of a diamond-like carbon (DLC) supplier in order to allow tribological results at different length scales and conditions to be collaboratively compared between the laboratories. Films will be deposited on Si wafers and will be delivered in the near future. Once results are obtained, a trip to exchange research results is planned.

Interactions with the MEMs community involved extensive discussions with Dr. Martin de Boer of Sandia National Laboratory. This interaction and contact, involving a description of research results to date and current practices in the lubrication of MEMS, will provide opportunities for additional exchange directly with one of the largest MEMS development efforts presently in this country.

Collaboration with Prof. Xiaoyang Zhu of the Department of Chemistry at the University of Minnesota has provided access to novel procedures for thin film deposition on Si substrates that promise applicability within existing MEMS technology as well as improved friction properties.

Collaborations with Prof. Gobet Advincula and Prof. Steve Baldelli are exploring the application of a range of surface vibrational probes to the study of SAMs on Si.

**Contacts:**

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Sandia National Laboratories  
Albuquerque, NM 87185

Dr. Xiaoyang Zhu  
Department of Chemistry  
University of Houston

**8. New discoveries, inventions, or patent disclosures.**

**9. Honors/Awards:**

Prof. Scott S. Perry  
Tenure and Promotion to Associate Professor  
September 2000

Prof. Scott S. Perry  
Appointment to Editorial Board of Tribology Letters  
August 2001

Prof. Scott S. Perry  
University of Houston Award for Research Excellence and Scholarship  
Associate Professor Level  
April 2002

Prof. Scott S. Perry  
University of Houston

Promotion to Full Professor of Chemistry and Chemical Engineering  
2003

Mr. Gang Liang  
Graduate Research Award sponsored by the Houston Section of the Society for  
Tribologist and Lubrication Engineers  
University of Houston  
2003